

Partial Molar Quantities and Their Physical Significance

In a multicomponent system, the contribution made by each component to an extensive thermodynamic property is known as its **partial molar quantity**. Since properties such as volume, enthalpy, entropy, Gibbs free energy, and internal energy depend on the amount of each component present, the addition of one mole of a substance changes these properties by a certain amount. This change is called the partial molar property of that component. Partial molar quantities are particularly useful in the study of solutions because the behavior of a component depends not only on its own amount but also on its interaction with other components present in the mixture.

Definition

The partial molar quantity of a component is defined as the change in an extensive property of the system when one mole of that component is added while keeping temperature, pressure, and the amount of all other components constant.

Mathematically, if X is any extensive thermodynamic property, then the partial molar property of component i is given by

$$\overline{X}_i = \left(\frac{\partial X}{\partial n_i} \right)_{T, P, n_j}$$

where,

- $\overline{X}_i$ = Partial molar property of component i
- X = Extensive thermodynamic property
- n_i = Number of moles of component i
- T = Temperature (constant)
- P = Pressure (constant)
- n_j = Number of moles of all other components (constant)

Total Property of a Mixture

The total extensive property of a mixture is equal to the sum of the products of the number of moles of each component and its corresponding partial molar property.

$$X = \sum_i n_i \bar{X}_i$$

For a binary solution containing components A and B,

$$X = n_A \bar{X}_A + n_B \bar{X}_B$$

Partial Molar Volume

Partial molar volume is the increase in the total volume of a solution when one mole of a component is added at constant temperature and pressure while keeping the amount of other components constant.

$$\bar{V}_i = \left(\frac{\partial V}{\partial n_i} \right)_{T, P, n_j}$$

Partial Molar Gibbs Free Energy

The partial molar Gibbs free energy is one of the most important partial molar quantities because it is equal to the chemical potential of the component.

$$\mu_i = \bar{G}_i$$

Thus,

$$\mu_i = \left(\frac{\partial G}{\partial n_i} \right)_{T, P, n_j}$$

Physical Significance

- Describes the contribution of each component to the total property of a mixture.
- Explains non-ideal behavior of solutions.
- Helps determine chemical potential.
- Used in phase equilibrium calculations.
- Essential for studying electrolyte and non-electrolyte solutions.
- Important in chemical engineering and industrial process design.
- Useful in calculating mixing properties and excess properties.

Characteristics of Partial Molar Quantities

- They are intensive properties.
- They depend on temperature, pressure, and composition.
- Their values change with concentration.
- For pure substances, the partial molar property becomes equal to the corresponding molar property.

Applications

- Determination of chemical potential.
- Study of solution thermodynamics.
- Calculation of activity and activity coefficient.
- Prediction of phase equilibria.
- Electrochemistry and electrolyte solutions.
- Industrial separation processes.

Key Formulae

Partial molar property:

$$\overline{X}_i = \left(\frac{\partial X}{\partial n_i} \right)_{T, P, n_j}$$

Total property:

$$X = \sum_i n_i \bar{X}_i$$

Chemical potential:

$$\mu_i = \bar{G}_i = \left(\frac{\partial G}{\partial n_i} \right)_{T, P, n_j}$$